# Direct Ion-Selective Electrode Measurements

*The ion-selective electrode (ISE) technique can be used to measure a variety of species in solution, including hydrogen ion (pH), calcium, halides, cyanide, sulfide, redox potential, carbon dioxide, oxygen, ammonia, nitrate, perchlorate, and fluoborate. Indicator electrodes are also commonly used in potentiometric titrations. ISE also has applications in process monitoring.*

## Principle of Technique

In pH and other direct ISE measurements, the indicator electrode selectively responds to a species of interest. The potential generated (measured vs a reference electrode) is proportional to the activity of a chemical species. The response is calibrated with known solutions of analyte.

In Eh measurements with noble-metal electrodes, the measured redox potential is determined by the solution's dominant, reversible redox couple.

## Samples

***Form.*** Aqueous or nonaqueous solutions are required.

***Size.*** For pH and Eh, the minimum sample size is 1 mL. Other measurements require a 10-mL sample that contains at least $10^{-6}$ mole/L of analyte.

***Preparation.*** Solutions can be analyzed directly as received or after dilution. Buffers or moderators are sometimes added to improve specificity or remove interferences.

## Limitations

Measurements do not directly indicate the concentration of an analyte, but rather its *activity*. However, electrodes can be calibrated to report concentration directly. An ISE is analyte-specific and responds to the activity of a particular ion in solution.

Consequently, species bound as complex ions (or precipitates) are not measured.

High ratios of other species may interfere. For example, pH electrodes are sensitive to high levels of sodium. Precision and accuracy are usually 2 to 5% of the concentration measured.

## Estimated Analysis Time

After conditioning and calibration of electrodes, 0.5 to 1 h per sample is required for solutions.

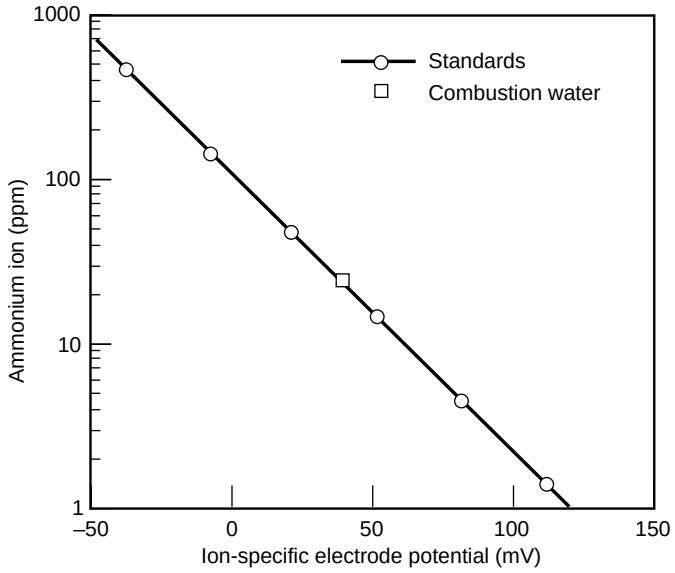
## Capabilities of Related Techniques

If a sufficient concentration of analyte is available, potentiometric titration using an ISE as detector is more accurate and precise (see titrimetry) than is a simple potentiometric determination referenced to calibration standards.

Ion chromatography is applicable to anions and can measure several simultaneously. It, too, is sensitive to speciation.

## Examples of Applications

- Measurement of pH, redox potential (Eh), and activity of oxygen in aqueous solutions and natural waters.
- Determination of sulfide ion in brines.
- Measurement of ammonia and cyanide in explosive combustion products.
- Measurement of low levels of halides such as fluoride in purified waters and solid leachates.




The mineral Buddingtonite contributes $NH_3$ to a flue gas condensate from low temperature combustion of charred oil shale, and the $NH_3$ is analyzed with an ammonium-specific electrode.

Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.